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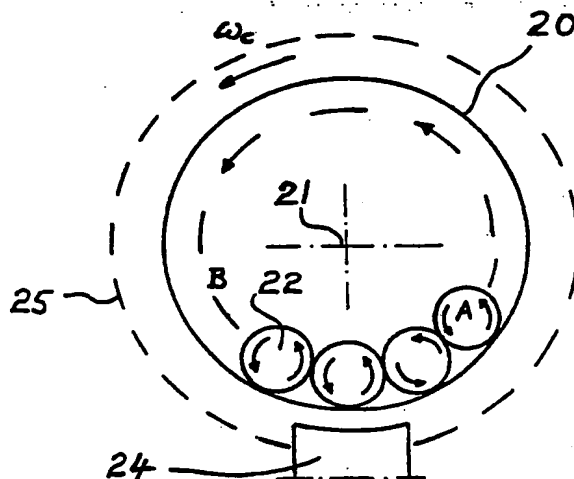
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<p>(21) International Application Number: PCT/AU90/00471</p> <p>(22) International Filing Date: 3 October 1990 (03.10.90)</p> <p>(30) Priority data: PJ 6646 3 October 1989 (03.10.89) AU</p> <p>(71) Applicant (for all designated States except US): THE AUSTRALIAN NATIONAL UNIVERSITY [AU/AU]; Acton, ACT 2601 (AU).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): NINHAM, Barry, William [AU/AU]; 18 Booth Crescent, Cook, ACT 2614 (AU). CALKA, Andrzej [PL/AU]; 178 Majura Avenue, Ainslie, ACT 2602 (AU).</p> <p>(74) Agents: DUNCAN, Alan, David et al.; Davies & Collison, 1 Little Collins Street, Melbourne, VIC 3000 (AU).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.</p> <p>Published With international search report.</p>

(54) Title: BALL MILLING APPARATUS AND METHOD, AND PRODUCTION OF METALLIC AMORPHOUS MATERIALS



(57) Abstract

A ball mill for use in mechanical alloying and grinding comprising a plurality of ferromagnetic balls (22) within a spherical or generally cylindrical chamber or cell (20) of a paramagnetic material. The cell has a substantially horizontal axis of rotation (21). At least one magnet (24) is mounted outside the chamber to produce a magnetic field within the chamber. The or each magnet is moveable between a plurality of locations on an arc (25) centred on the axis of rotation of the chamber. In mechanical alloying with a ball mill, the addition of a surfactant to the powder charge within the ball mill modifies the rate and nature of the reaction(s) within the mill. The surfactant should be added in a quantity sufficient to produce a monomolecular layer over the surface of the particles comprising the powder charge, and with an organic solvent, such as hexane. Metallic amorphous materials can be produced using the ball mill of the invention by (a) obtaining amorphous ribbons from a master alloy of the required chemical composition, (b) crystallising the ribbons by annealing at a temperature of about 600 °C, then (c) milling the crystallised ribbons in a slight overpressure of dry helium to produce a fully amorphous material.

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TITLE: "BALL MILLING APPARATUS AND METHOD, AND
PRODUCTION OF METALLIC AMORPHOUS MATERIALS"

Technical Field

This invention concerns ball milling and mechanical
5 alloying. More particularly, in a first aspect, it
concerns an improved ball mill for use in grinding
and in alloying (both low temperature alloying and
high temperature alloying). In a second aspect, it
concerns improved technique for wet milling of
10 powders, involving the addition of a surfactant. In
a third aspect, it concerns the production of
amorphous materials from crystallised metallic glass
ribbons by mechanical alloying.

Background to the Invention

15 Ball mills and attritors have been used for many
years to produce fine powders. In ball mills, the
energy input to the powder charge is provided by the
rotation of the mill, a cylindrical cell or vial
about a horizontal axis, so that hard balls within
20 the mill are tumbled with, or onto, the charge in the
mill. In attritors, metal arms are used to stir the
ball charge.

As noted by Y S Benjamin in his article in Scientific
American, volume 234, page 40 (1976), it was
25 appreciated in the early 1970's that in addition to
creating powders, ball milling could be used to
produce solid state reactions which result in the
synthesis of new alloys from elemental powders. It

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was also discovered that ball milling can modify an alloy structure. The first of these techniques (the synthesis of alloys) is known as "mechanical alloying"; the second technique has been termed
5 "mechanical grinding".

When mechanical alloying is used to produce new materials, there is a combination of repeated welding, fracturing and rewelding of a mixture of powder particles having a fine microstructure
10 together with a rapid interdiffusion process.

Both mechanical alloying and mechanical grinding have been effected using either the vibrating milling technique or the rotating milling technique. In vibrating-frame mills, hardened steel balls are
15 caused to impact substantially vertically upon the powder charge. Local overheating of the particles can occur as a consequence of the mill structure. This local overheating is difficult to remove. In addition, the mixing of the particulates is very slow
20 (and in some designs of mill, is almost non-existent). Thus rotating mills, in which the steel balls roll along a circular arc on the inner wall of the mill chamber or vial, are preferred for mechanical alloying.

25 In rotating mills, the powder charge is spread on the inner surface of the chamber. This ensures that heat generated within the chamber is removed by conduction through the cylindrical wall of the

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chamber and that there is effective mixing of the powder constituents. However, when using rotating mills, it is not possible to provide the impact energy of the balls that is achieved in 5 vibrating-frame mills when a rotating ball mill is used.

Some alloys have been difficult to fabricate using ball milling techniques because the ball milling produces excessive cold welding of the components 10 being milled. For example, when ball milling is used to produce alloys containing aluminium and magnesium, the cold welding results in the production of lumps of alloyed material, which act to suppress the solid state reactions. Some success in overcoming this 15 problem by the use of organic solvents has been reported by P S Gilman and W D Nix in their paper in Metallurgical Transactions, volume 12A, page 813 (1981). The use of organic solvents as lubricants by Gilman and Nix enabled them to achieve a balance 20 between cold welding and fracturing, and to keep the particle size small and within a narrow size distribution. Nevertheless, wet milling of aluminium and magnesium powders, and other powders which exhibit excessive cold welding when dry milled, has 25 had only limited success in mechanical alloying.

Problems are also experienced when a mixture of titanium and carbon powders, or a mixture of aluminium and titanium powders are ball milled. These powder mixtures, when ball milled, form

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"nanostructures" (powders with a mean particule size of the order of 100 nanometres) which oxidise explosively when exposed to air or other oxygen-rich atmospheres.

5 A further problem, that is encountered particularly when the mechanical alloying or the production of very fine powder requires long ball milling times, is the contamination of the product alloy or powder with particles from the steel balls used in the ball mill.

10 Metallic amorphous materials have a combination of mechanical, chemical and magnetic properties which indicate that they have a good potential for industrial exploitation. Among their beneficial
15 mechanical properties are high ductility, strength and hardness. Some metallic amorphous materials show excellent corrosion resistance. The magnetic softness exhibited by many metallic amorphous materials is particularly important in various magnetic applications.

20 Metallic amorphous materials have been manufactured using (a) rapid quenching from a melt, (b) vapour deposition, and (c) electrochemical processes. Most metallic glasses (glass here means amorphous, or non-crystalline material) have been manufactured in
25 ribbon form by rapid quenching from a melt using a single roller quenching technique. The thickness of

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these ribbons is limited by cooling rates and can vary from about 10 micrometres to about 80 micrometres.

For industrial applications there is a necessity to produce bulk glassy alloy structures. Several methods have been used to consolidate metallic glass ribbons. Cold and warm pressure consolidation, ultrasonic welding, explosive welding, and dynamic compaction have all be used to convert these special alloys into bulk form. However, all of these consolidation methods are still in an experimental stage and most metallic amorphous materials are produced in the powder form.

Among the methods for manufacturing amorphous powders are (a) direct casting from the melt using a modified roller technique, (b) the spark erosion method, (c) a gas-water atomization process, (d) sputtering and (e) plasma spray deposition methods. These methods all have associated disadvantages, such as the production of undesirable particle shapes (flakes, rough spherical or highly irregular particles with a wide range of sizes varying from 1 micrometre to 40 micrometres) and/or the limited quantity of material that can be produced. Thus there has been only limited successful production of powders which are entirely amorphous.

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Disclosure of the Present Invention

It is an objective of the first aspect of the present invention to provide an improved ball mill in which the impact energy of the vibrating-frame mill technique can be achieved while the cooling and powder mixing features of the rotating mill technique are maintained. It is a further objective of the first aspect of the present invention to provide a ball mill in which the energy or intensity of the milling process is variable and controllable.

These objectives are achieved by constructing the cylindrical chamber of a rotating ball mill from a paramagnetic material and mounting at least one magnet outside the chamber in a manner such that either (i) the magnet (or magnets) can be moved around the chamber along an arc centred on the axis of rotation of the chamber, or (ii) the location of the magnet (or magnets) can be varied between a number of mounting positions, each located on an arc centred on the axis of rotation of the chamber. Mounting a magnet (or magnets) in this manner creates a perturbation of the normal movement of the steel balls of the ball mill when the chamber is rotated. In particular, when a magnet is positioned vertically below the chamber, there is an increase in both the rotation of the balls in the chamber and their contact time with the powder charge of the chamber. As the magnet is moved to a position high on one side of the chamber, each ball is lifted by the magnet before being dropped on to the charge (including

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other balls) of the mill, to provide a high energy impact. At intermediate positions of the magnet around the chamber, the steel balls provide a combination of increased impact energy and increased contact with and mixing of the powder charge in the mill.

Thus, according to the first aspect of the present invention, there is provided a ball mill comprising:

- 10 (a) a substantially spherical or generally cylindrical chamber, the chamber being mounted (i) in the case of a substantially spherical chamber, for rotation about a substantially horizontal axis, and (ii) in the case of a
15 generally cylindrical chamber, with the axis of the cylinder substantially horizontal and for rotation about the axis of the cylinder; and
- (b) a plurality of steel balls within the chamber; characterised in that
- (c) the chamber is made of a paramagnetic material;
- 20 (d) the steel of which the balls are made is a ferromagnetic material; and
- (e) at least one magnet is mounted outside the chamber, said or each magnet (i) having lines of magnetic force which penetrate into the chamber,
25 and (ii) being moveable between a plurality of locations along an arc having its centre of curvature substantially at the axis of rotation of the chamber.

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As noted above, and as will be explained in more detail later in this specification, the magnet (or magnets) may be either mounted for movement along an arc having its centre of curvature at the axis of
5 rotation of the chamber, or repositionable at a plurality of discrete locations around the chamber, each of the discrete locations being on an arc having its centre of curvature substantially at the axis of rotation of the chamber.

- 10 The magnet (or each magnet) may be an electromagnet or a permanent magnet.

It is an objective of the second aspect of the present invention to provide a method of wet milling which permits the mechanical alloying of powders of
15 aluminium and magnesium, and other powders which tend to produce lumps when dry milled, due to excessive cold welding. It is a further objective of the second aspect of the present invention to provide a method by which powders which normally form
20 nanostructures upon ball milling and explosively oxidise when exposed to air can be safely ball milled. It is yet another objective of the second aspect of the present invention to provide a ball milling method in which contamination of the milled
25 material by the material of the steel balls of the mill is reduced.

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These objectives of the second aspect of the present invention are achieved by wet ball milling the material being milled, and adding to the mill a surfactant material, usually in an organic solvent.

5 The amount of surfactant added should be sufficient to provide a monomolecular layer of surfactant over the entire surface of the material being ball milled. Some control over the nature of the final product of the ball milling can be achieved by selecting a

10 particular surfactant from a group of alternative surfactants. The use of surfactants in wet ball milling, however, is not limited to the ball milling of problem powders, or long ball milling likely to produce undesirable contamination of the milled

15 product.

Thus, according to the second aspect of the present invention, there is provided a method of wet ball milling a material in a ball mill, characterised by the addition to the material of sufficient surfactant

20 to coat the surface of the material with a monomolecular layer of the surfactant.

Normally an organic solvent, such as hexane, will also be added to the ball mill with the surfactant.

Both cationic and anionic surfactants may be used.

25 Among the preferred surfactants are:

- (a) sodium-1,2 bis (dodecyl carbonyl) ethane-1-sulfonate;

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(b) lithium-1,2 bis dodecyloxycarbonyl
sulfasuccinate;

(c) didodecyldimethyl ammonium bromide;
and

5 (d) ammonium dihexadecyl dimethylacetate.

The wet ball milling may be performed in a ball mill constructed in accordance with the first aspect of this invention, or it may be performed in a conventional ball mill.

10 It is an object of the third aspect of the present invention to provide a method for the manufacture, in relatively large quantities, of metallic amorphous materials.

This objective is achieved by a method comprising the
15 steps of:

- (a) producing a master alloy having the chemical composition of the required amorphous material;
- (b) producing amorphous ribbons of the master alloy;
- (c) annealing the amorphous ribbons to convert them
20 into crystalline form; then
- (d) ball milling the crystalline material for a period sufficient to produce a fully amorphous powder.

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Steps (a) and (b) involve well known techniques. The annealing step (c) is preferably performed under vacuum at a temperature of about 600°C, for a period in the range of from 10 minutes to 20 minutes. The milling step is preferably carried out in a slight overpressure of an inert gas (e.g. helium or argon), using a ball mill constructed in accordance with the first aspect of the present invention, but conventional ball mills may be used for step (d).

10 For a better understanding of the present invention, embodiments of the first, second and third aspects of the invention will now be described, by way of example, with reference to the accompanying drawings.

Brief Description of the Drawings

15 Figure 1 is a schematic diagram of a conventional ball mill.

Figure 2 illustrates a ball mill constructed in accordance with the present invention, with a single magnet located beneath the chamber of the ball mill.

20 Figures 3 and 4 show the ball mill of Figure 2, with the magnet in different locations along the arc of movement of the magnet.

Figure 5 depicts a ball mill with two magnets, on diametrically opposed locations around the chamber, 25 one magnet being directly above the chamber and the other magnet directly below the chamber.

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Figures 6 and 7 are x-ray diffractograms of different powder mixtures using the ball mill of Figures 2 to 5.

Figure 8 is a collection of x-ray diffractograms of the product of mechanically alloyed elemental mixtures of aluminium and magnesium in the proportions $Al_{50} + Mg_{50}$, under different ball milling conditions.

Detailed Description of the Embodiments

- 10 The conventional ball mill shown in Figure 1 has a cylindrical cell or chamber 10 mounted for rotation in the direction of arrow A about a horizontal axis 11. A plurality of steel balls 12 within the chamber are tumbled with the powder charge in the cylinder.
- 15 Access to the chamber is through an end door 13. The operation of this type of ball mill is well known and further explanation here of its mode of operation is unnecessary.

The ball mills illustrated in Figures 2 to 6 each have a cylindrical or spherical cell 20 made from a hard paramagnetic alloy. The precise shape of the cell or chamber 20 is not important. The chamber 20 is rotatable about a substantially horizontal axis 21 which, in the case of a cylindrical or generally cylindrical chamber, is also the axis of the chamber. Within the cell are a number of balls 22, made from a hard ferromagnetic alloy. At least one magnet 24, which may be an electromagnet or a permanent magnet,

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is mounted outside the cell 20 but close enough to the cell for the field of the magnet to have a significant influence upon the ferromagnetic balls 22.

5 As will be apparent from Figures 2 to 6, the magnet or magnets 24 can be repositioned relative to the chamber 20 either by movement around an arc which has its centre of curvature substantially coincident with the axis of rotation 21 of the chamber 20 or by
10 physically moving the or each magnet from one discrete mounting location to another of a number of discrete mounting locations which are provided adjacent to the chamber 20.

The present invention may be used with a single layer
15 of the balls 22 or the chamber 20 may contain a large number of ferromagnetic balls.

When a powder charge is loaded into the chamber 20, the powder will rapidly become uniformly distributed on the internal surface of the cell 20, with a layer
20 of powder also on the balls 22. The mode of operation of the ball mill depends upon the required result.

If the magnet 24 is positioned immediately below the chamber 20 as shown in Figure 2, the magnetic field
25 established by the magnet 24 holds the balls 22 in the bottom part of the cell 20. Friction between the surface of the balls and the inner wall of the cell

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20 causes the balls 22 to rotate in the same direction with a frequency w_b given by the relationship

5
$$w_b = w_c \cdot \frac{R}{r}$$

where w_c is the rotational frequency of the cell, r is the radius of the balls 22 and R is the internal radius of the cell or chamber 20. Periodically, the outer ball 22 on the right side of the assembly of 10 balls in the chamber breaks away from the pack of balls and, under the influence of centrifugal forces, performs an almost complete circular transit, along the path 28 while in contact with the inner wall of the chamber 20, to the other side of the pack of 15 balls. At the end of this transit, it strikes the outer-most ball on the left side of the pack of balls.

In this mode of operation, the powder charge in the ball mill is worked both by impact and by a shearing 20 action.

The balls 22 may be confined to the bottom part of the chamber 20 for the entire milling process by either (i) increasing the intensity of the magnetic field applied by the magnet 24, or (ii) decreasing 25 the frequency of rotation of the chamber or cell 20. In this operating mode, the balls in the chamber both rotate and oscillate around their equilibrium

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position at the bottom of the cell 20. The powder charge in the mill, therefore, is worked mostly by shearing. This is the "low energy" mode of the ball mill. In this mode, the magnetic field of the magnet 5 24 causes the balls to apply a greater force to the layer of powder on the inner surface of the chamber 20 than is applied in a conventional ball mill. In addition, the contact time between the balls is increased. This results in a more effective 10 fracturing process. Thus little welding of the constituents of the powder charge is effected in this mode of operation. However, this mode of operation of the present invention is characterised by very good mixing of the powder particles and low local 15 temperatures, which is useful for grinding materials to reduce their particle sizes or (in the case of alloy particles) to modify their structure. This mode of operation is also useful for low temperature alloying - particularly the alloying of low melting 20 point alloys (for example, aluminium base alloys), which leads to extended solid solubility.

If, as shown in Figure 5, a second magnet 29 is positioned diametrically opposite the magnet 24 of Figures 2 and 3, the circular path of each break-away 25 ball (under centrifugal force) is halted at the highest point inside the cell. A ball trapped by the magnetic field of the magnetic field of the magnet 29 in the uppermost position within the cell can be released to fall vertically on to one of the 30 ferromagnetic balls in the mass at the lower-most

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part of the chamber or cell. When this occurs, the two colliding balls are rotating in opposite directions at the point of impact, which results in a combination of shearing and uniaxial pressure at the surface of contact. This is the "high energy" mode of operation of the ball mill.

Two different modes of operation of the ball mill of the present invention are shown in Figures 3 and 4. By repositioning the magnet 24 and by reducing the cell rotation frequency to a value lower than the cell rotation frequency of the cell 20 when the mill is operated in the Figure 2 or Figure 5 mode, whenever a ball 22 is released from the mass of balls at the lower-most region of the cell, the released ball is not held continuously against the inner wall of the cell by centrifugal force. Instead, the released ball follows an arcuate path in which the ball is partly out of contact with the cell wall and another ball, and then strikes either one of the bottom balls (as shown in Figure 3) or the opposite portion of the cell wall (as shown in Figure 4).

When operating in the mode shown in Figure 3, each break-away ball which has descended from the top of its path to strike a lower ball has a high rotational speed in the opposite direction to the lower ball. This is essentially the same mode of operation as that shown in Figure 5. The impact results in a significant increase in the local temperature at the point of impact, to facilitate the effective

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synthesis of high melting point alloys and intermetallic phases (such as TiB_2 , $AlPd$, Al_3Pd_5) and an extension of solid solubility in high temperature alloys (such as titanium in silicon).

5 In the mode of operation illustrated in Figure 4, the magnet 24 is raised higher than in the mode of operation illustrated in Figure 3. However, the Figure 4 mode of operation is comparable to the mode of operation shown in Figure 2. The ball descending
10 from the point of highest lift strikes the internal surface of the chamber, which is rotating in the same direction as the surface of the ball. Thus the local temperature produced on impact is higher than in the mixing and grinding mode of operation but lower than
15 in the mode of operation shown in Figures 3 and 5. The mode of operation shown in Figure 4 is thus particularly suitable for medium melting point reactions, with subdued alloying. There is a combination of, or balance between, welding and
20 fracturing. Amorphization of alloys (for example, magnesium-zinc alloys) and extension of solid solubility and creation of intermetallic phases at low and average melting point elements or alloys (such as aluminium-magnesium, aluminium-iron and
25 magnesium-zinc) can be achieved.

Using a ball mill constructed in accordance with the present invention, and operated in the mode illustrated in Figure 3, the alloy $AlPd$ was obtained by the following method. Elemental powders of

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aluminium and palladium, having a purity of 99.99 per cent and a grain size of about 20 micrometres were milled for 66 hours in a slight overpressure of pure, dry helium. X-ray diffraction patterns obtained from the mechanically alloyed powders after different periods of milling showed the following: after milling for 45 hours, the intermetallic phase AlPd was observed and after 66 hours of milling, the mixture contained no detectable amount of elemental aluminium or palladium. However, a small quantity of the alloy Al_3Pd_5 was detected after 66 hours of milling. It is believed that the Al_3Pd_5 alloy may be due to the presence of a small amount of elemental aluminium powder being deposited on the mill walls during the milling process, so that the remaining powder became aluminium-depleted, and thus rich in palladium.

An investigation by the present inventors of the operating parameters of the ball mill of Figures 2 to 6 has shown that, when the ball mill of the present invention is in use, the major milling parameters are as follows;

collison time:	6.5×10^{-5} sec.
Hertz radius:	4.6×10^{-4} m.
Maximum impact stress:	37 Kbar.

These values are close to the corresponding values quoted for commercial vibrating mills. Thus the energy per impact in the ball mill of the present

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invention is comparable to the energy per impact of other devices. A significant feature of the ball mill of the present invention, however, is that in every mode of operation, the ball movement pattern is well defined and highly reproducible. This contrasts with the chaotic and generally unpredictable ball movement characteristics of most conventional milling devices.

In a further example of the use of the ball mill of the present invention, the mill was used to produce the amorphous phase of nickel-zirconium mixtures. Other workers have shown that the amorphisation of these mixtures, using different milling equipment, occurs by two paths. The amorphous phase is formed directly when either the vibrating frame or a Fritsch "Pulverisette 5" planetary mill is used, but a crystalline intermetallic phase forms initially when a different type of planetary mill is employed. In addition, it has been shown that changing the milling intensity and using different combinations of the planetary mill rotation patterns can influence the outcome of the milling.

The present inventors have produced the alloy $\text{Ni}_{62}\text{Zr}_{38}$ by both of the amorphisation paths, using two different modes of operation of the ball mill of the present invention. When the high-energy mode of Figure 3 was used, the amorphous phase was formed directly from a powder mixture of the indicated atomic percentages of nickel and zinc. X-ray

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diffraction revealed that during the milling process, the intensity of diffraction peaks due to the elemental zirconium and nickel decreases, while a peak corresponding to the amorphous phase of the intermetallic material develops. The x-ray diffraction pattern after 60 hours of milling is shown as trace A in Figure 6.

When the low-energy milling mode described above was used to mill the elemental powder mix, the crystalline intermetallic material was formed first, then was transformed into the amorphous phase. An x-ray diffraction pattern of the milled material after 180 hours of milling is shown as trace B in Figure 6. After continuing the milling until the elemental powder had been milled for 240 hours, some traces of the crystalline phase remained visible on top of the amorphous phase peak of the x-ray diffraction pattern.

The nature of alloys of titanium and boron formed by mechanical alloying are also influenced significantly by the milling conditions under which they are generated. Figure 7 shows two x-ray diffractograms obtained from ball milling mixtures of the nominal composition of 33 atomic per cent of titanium and 77 atomic per cent of boron. The upper trace, trace A, was obtained from a sample milled for 80 hours using the ball mill of the present invention operated in the high energy milling mode of Figure 3. This is the x-ray diffraction pattern of the pure TiB_2 phase.

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The lower trace, trace B, was obtained from a sample milled for 80 hours in the same ball mill, with the same rotational frequency of the chamber of the mill, but with no magnetic field influencing the balls within the chamber (that is, the sample was milled in a conventional ball mill under notionally identical conditions). The lower diffractogram of Figure 7 shows the presence of a mixture of crystalline titanium and a small amount of TiB_2 . Continuing the milling in the "conventional" ball mill until the powder charge had been milled for 400 hours failed to produce a product of pure TiB_2 .

In other experiments using the ball mill of the present invention operating in the Figure 3 mode, powders of silicon and titanium (having a purity of 99.98 per cent and a mean grain size of about 20 micrometres) were milled in an atmosphere of dry helium to produce the alloys Ti_5Si_3 and $TiSi_2$. The former alloy was obtained in the amorphous form, the latter in crystalline form. Similar experiments with the mill operated in the Figure 4 mode produced highly reproducible solid solutions of up to 20 per cent titanium in silicon (this is remarkable in view of the conventional understanding that there is no solid solubility of titanium in silicon in the equilibrium state).

The present inventors have also used the ball mill of the present invention to perform amorphization of crystalline alloys. In one experiment, the

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magnesium-zinc alloy $Mg_{70}Zn_{30}$ was milled in the ball mill of the present invention, operated in the Figure 2 mode of operation. The $Mg_{70}Zn_{30}$ alloy was prepared from 99.99 per cent purity components, which were
5 melted in a tantalum crucible enclosed in a fused silica capsule. The melting was performed in an atmosphere of pure helium. The product alloy was crushed into small pieces and those pieces were milled in the ball mill of the present invention, in
10 the Figure 2 operating mode, with the chamber rotating at the rate of 200 revolutions per minute. Again, a slight overpressure of pure, dry helium was present in the chamber of the mill.

Samples of the milled powder were extracted at
15 various stages during the milling and subjected to x-ray diffraction analysis. Initially, the master alloy was shown to be a mixture of crystalline phases of magnesium, $MgZn$ and (traces only) $Mg_{51}Zn_{20}$. Continued grinding resulted in a decrease in the
20 peaks in the x-ray diffraction pattern due to the crystalline components and the appearance of a broad peak due to the appearance of the amorphous phase. A steady state situation was achieved after 40 hours of grinding, with no change in the x-ray diffraction
25 pattern after further grinding under the same conditions. However, further amorphization was obtained by an additional 17 hours of mechanical grinding with the mill operating under the lower energy conditions of 50 revolutions per minute.

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Use of Rutherford backscattering and electron microprobe techniques to analyse the amorphous powder showed that the product powder contained the composition $Mg_{69}Zn_{30}Si_1$ or $Mg_{67.5}Zn_{32.5}$. The 5 different compositions were estimated from the different analysis techniques. No iron or chromium contamination of the alloy from the ball mill was detected. It was concluded that the mechanical grinding had synthesised a binary magnesium alloy.

- 10 A recent modification of the ball mill of the present invention is the inclusion of means to heat the mill during the milling process, to modify the rate and nature of the reaction(s) within the ball mill.

The ball mill of Figures 2 to 5 has also been used to 15 demonstrate the benefits of including a surfactant in the ball milling process, particularly in the production of aluminium-magnesium alloys. However, it is emphasised that the second aspect of the present invention is not limited in its application 20 to milling performed in the ball mill of the present invention.

Surfactants are amphiphillic molecules composed of a hydrophillic moiety or headgroup which is coupled chemically to a hydrophobic moiety or tail. The tail 25 is typically a hydrocarbon chain, or is predominantly a hydrocarbon, but it may comprise any other hydrophobic group of molecules (for example, fluorocarbons). The surfactant molecule may contain

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one or more chains coupled to the headgroup. The headgroup may be non-ionic (for example, a poly-oxyethylene, which is electrically neutral), zwitterionic (where the net electrically neutral charge on the headgroup is separated by atomic dimensions to form an electrical dipole), or it may be ionic. An ionic surfactant is preferred for the second aspect of the present invention.

Ionic surfactants may have a positive charge on the headgroup (in which case they are cationic, or they may have a negative charge (anionic). They carry with them free counterions of the opposite charge (for example, Br^- or Na^+).

The results obtained by the present inventors have shown a weak dependence on the size of the tail, which can be varied to optimise the efficiency of the ball milling (for example, the tail may be selected from dodecyl, decyl and hexadecyl trimethyl ammonium bromide). The results obtained also vary with the charge, the counterion, the degree of hydration (bound water), and the amount and kind of lubricant (usually termed an "oil") added to the surfactant. Typical lubricants are hexane and decane. The added "oil" affects not only the grinding, cracking and the particle size produced during ball milling, but also the surface activity of the surfactant. It is essential in enhancing solid state reactions involved in the alloying process.

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In general, non-ionic or weakly ionic surfactants (such as oleic acid and sodium stearate) will have little effect in the enhancing of desired solid state reactions.

5 In this specification the term "surfactant" includes polymers which may have an ionic character.

Non-ionic surfactants which have the property of chelating charged ions (for example, Zn^{++} , Cu^{+++} and V^{5+}) can be used to deliver desired additional
10 elements.

The amount of surfactant used, and its type, affects

- (a) the speed of grinding or of a solid state reaction (for example, the amorphisation of TiB, which requires 80 hours of milling without a
15 surfactant, is completed in 30 hours of milling if an ionic surfactant is added to the charge in the mill);
- (b) the shape of nanoparticles produced (for example, nanoparticles of CoSiB can be almost
20 spherical or needle-like, depending upon the surfactant added when the CoSiB particles are milled);
- (c) the particle size of the milled product; and
- (d) the nature of the product of the milling (some
25 inorganic materials, such as a mixture of zinc sulphide, silica and zirconium can be milled together to produce quartz, amorphous silica or zeolites; it is also possible to obtain either

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zirconia and zeolite, or zirconia and amorphous silica when $\text{ZrO}_2 \cdot \text{SiO}_2$ is milled with different surfactants).

When using surfactants in milling, the present
5 inventors have produced new equilibrium phases not hitherto accessible, and metastable phases (which can, in fact, be equilibrium structures). A typical example is the production of the alloy $\text{Al}_{50}\text{Mg}_{50}$ by milling an aluminium and magnesium powder mixture
10 with the cationic surfactant, didodecyl dimethyl ammonium bromide.

Although, as noted above, the amount of surfactant added to the charge of a ball mill affects the product of the milling, the surfactant should be
15 added in sufficient quantity to form at least a monomolecular layer of surfactant around the particles being milled.

The value and effectiveness of the second aspect of the present invention will be apparent from the
20 following examples of the effect of the addition of a surfactant to the charge of a ball mill.

Aluminium-magnesium alloys produced by conventional ingot metallurgy have a maximum solubility of magnesium in aluminium of about 28.9 per cent at a
25 eutectic temperature of 450°C . At a temperature of 100°C , the maximum solubility of magnesium in aluminium is only 2.1 per cent. Rapid quenching of

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the higher temperature composition has yielded room temperature alloys having a maximum solubility of about 15 per cent of magnesium in aluminium. Nevertheless, the rapidly quenched alloys are characterised by high strength, good corrosion resistance and low density. It has been believed that mechanical and chemical properties of aluminium-magnesium alloys will be enhanced if the maximum solid solubility of magnesium in aluminium could be increased and the grain size of the alloy could be decreased.

In a series of experiments, mechanical alloying in the ball mill of the present invention was effected with the mill operated in the mode shown in Figure 4. Pure powder mixtures in quantities sufficient to produce the alloys $\text{Al}_{70}\text{Mg}_{30}$, $\text{Al}_{50}\text{Mg}_{50}$ and $\text{Mg}_{70}\text{Al}_{30}$ were used in the ball mill, which was operated to perform (a) dry milling in a helium atmosphere and (b) wet ball milling with a surfactant mixed with a hydrocarbon fluid. The results obtained by the series of experiments are summarised in Table 1. In Table 1, S1 is the anionic double chained surfactant didodecyl sodium sulfosuccinate and S2 is the cationic double chained surfactant didodecyl dimethyl ammonium bromide. In each experiment in which surfactant was used, from 0.5 to 2 molecular per cent of surfactant was added per total number of aluminium and magnesium atoms. Other experiments showed that with hexane alone in the wet milling operation, or

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with any other neutral hydrocarbon in the wet milling process, the result achieved with the addition of a surfactant cannot be obtained.

TABLE 1

5	Powder Composition	Milling Environment	Obtained Alloy Structure
	$\text{Al}_{70}\text{Mg}_{30}$	Dry + helium	Al_2Mg
	$\text{Al}_{70}\text{Mg}_{30}$	S1 + hexane	17% Mg in Al
	$\text{Al}_{50}\text{Mg}_{50}$	Dry + helium	Al_2Mg_3 + BAlMg
10	$\text{Al}_{50}\text{Mg}_{50}$	S1 or S2 + hexane	Al_2Mg_3 + 30% Al
	$\text{Mg}_{70}\text{Al}_{30}$	Dry + helium	Al_2Mg_3 + Al_2Mg
	$\text{Mg}_{70}\text{Al}_{30}$	S1 + hexane	Al_2Mg_3 + 34% Al

It will be seen from the results presented in Table 1 that mechanical alloying of aluminium and magnesium
 15 powders results in the formation of equilibrium intermetallic phases. In the presence of the surfactant, however, there is a tendency to form extended solid solutions of magnesium in aluminium.

Heating the alloys produced in a calorimeter showed
 20 that the solid solutions of magnesium in aluminium, formed by wet milling in the presence of a surfactant, are stable up to the melting point of the alloy. Annealing a sample of $\text{Al}_{50}\text{Mg}_{50}$ alloy by wet milling (produced with a surfactant present) at 400°C
 25 for two hours revealed no precipitation of magnesium

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from the alloy. In contrast, the alloys produced by ball milling in a dry helium atmosphere exhibited very low stability when heated, with a tendency for fast grain growth and recrystallisation from the alloy towards equilibrium structures that were absent from the samples prepared using wet milling with a surfactant present.

In other experiments, which demonstrate how different results can be achieved using different surfactants, 10 powders mixed to produce the alloy $\text{Al}_{50}\text{Mg}_{50}$ were milled for 160 hours under different conditions. The results obtained were as follows:-

1. When no surfactant was added to the charge in the mill, the x-ray diffraction pattern shown as trace A of Figure 8 was obtained. The diffraction peaks are very broad, indicating an amorphous-like structure. After annealing for 5 minutes to 350°C , the milled product structure transformed into a mixture of two equilibrium phases, $\beta(\text{Al}_3\text{Mg}_2)$ and $\gamma(\text{Al}_{12}\text{Mg}_{17})$.
2. When the surfactant sodium-1,2 bis (dodecyl carbonyl) ethane-1-sulfonate was added to the charge in the ball mill, the x-ray diffraction pattern shown as trace B of Figure 8 was obtained. This diffractogram shows the presence of fcc aluminium, plus a solid solution of 24 atomic per cent magnesium in aluminium, plus a small amount of the equilibrium phase $\text{Al}_{12}\text{Mg}_{17}$.

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3. After 160 hours of milling with the surfactant lithium-1,2 bis dodecyloxycarbonyl sulfasuccinate added to the powder charge in the ball mill, the product had the x-ray diffraction pattern shown by trace C in Figure 8. This trace shows two strong and broad peaks, indicating the presence of a bcc structure characterised by a lattice parameter $a = 4.15$ Angstrom units. A small amount of fcc aluminium can also be identified. The product phases were very stable on heating up to 360°C .
4. When the surfactant didodecyldimethyl ammonium bromide was the added surfactant, the product after 160 hours of milling had the diffraction pattern shown as trace D of Figure 8. This diffractogram shows the presence of the fcc aluminium phase and the bcc phase noted for trace C of Figure 8. The milled product was again stable when heated to 360°C .
- 20 The addition of a surfactant to a ball mill charge has also been shown to be beneficial when the mixture of powders being milled produces nanostructures or nanoparticles (very fine particles of diameter 100 nanometres or less). Nanostructures are characterised by a large percentage of the total number of atoms residing on the particle surface, instead of being in the bulk of the particle. The properties of nanostructures are largely affected by surface phenomena. In particular, when a

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nanostucture contains easily oxidisable elements, a violent (even explosive) reaction can occur on exposure to air or another oxygen-rich atmosphere.

The present inventors have shown that the addition of
5 sufficient surfactant to cover the surface of the nanoparticles with a monomolecular layer, when mixtures of powders of (a) carbon and titanium in the atomic proportions $Ti_{50} + C_{50}$, and (b) aluminium and titanium in the atomic proportions $Al_{50} + Ti_{50}$, are
10 milled, results in the production of particles which can be safely handled in air without further treatment. Normally, milling of such powder mixtures in the absence of a surfactant produces nanoparticles which oxidise explosively on exposure to air.

15 As indicated above, the addition of surfactants has been found to provide control over the size and shape of milled particles of some soft magnetic materials, such as $(Co-Fe)_{75}Si_{15}B_{10}$. Circular particles having a diameter of about 100 nanometres are produced when
20 particles of this soft magnetic material are ball milled in the presence of sodium-1,2 bis (dodecyl carbonyl) ethane-1-sulfonate. Needle-like particles having a length of about 100 nanometres are obtained when the surfactant added to the ball mill is
25 ammonium dihexadecyl dimethylacetate. The shapes of the product milled particles affected the values of the maximum saturation magnetisation and the anisotropy field of the soft magnetic materials.

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A common problem in ball milling, particularly when the milling is used to synthesise alloys, is the contamination of the milled product with the material of which the balls and cell of the mill are made.

5 The level of contamination depends on the type of ball mill used and the conditions under which the milling is effected. The average level of contamination recorded by the present inventors when using the ball mill of the present invention is about

10 1.0 atomic per cent, when synthesising alloys of silicon and titanium. (When forming magnesium zinc alloys, the contamination was below the detection level.) The present inventors have observed that when a surfactant is added to the particle charge of

15 a ball mill, the level of contamination by the material of the balls and cell of the ball mill of the product is significantly reduced - typically by at least a factor of 10.

In another series of experiments performed by the

20 present inventors, it was not possible to produce a solution of iron in aluminium at room temperature by using conventional ball milling. With wet ball milling in the presence of a surfactant, solid solutions of iron in aluminium were obtained at room

25 temperature, with the iron being present in the solution at up to 7 atomic per cent.

It is not yet understood why surfactants enhance metal solubility in mechanical alloying with a ball mill. It is suggested that a lowering of the surface

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energy and the production of changes in surface molecule stoichiometry may be involved. Alternatively, a change in the surface molecule lattice spacing, allowing interdiffusion of 5 components, may be responsible. The presence of intense electric fields at the particle surface, caused by the electrically charged surfactant headgroup, is believed to affect the surface properties of the powder particles when ionic 10 surfactants are used.

In a realisation of the third aspect of the present invention, an alloy (a master alloy) of the composition $\text{Co}_{70.3}\text{Fe}_{4.7}\text{Si}_{15}\text{B}_{10}$ was prepared from high purity elements in an arc furnace under an atmosphere 15 of high purity argon. Amorphous ribbons of the master alloy were spun from a quartz crucible on a single steel wheel in an atmosphere of air. The ribbons typically had a width of about 15 mm and a thickness of about 35 micrometres. The amorphous 20 ribbons were fully crystallised by annealing in vacuum at a temperature of 600°C for between 10 minutes and 20 minutes.

The crystallised ribbons were then milled in a ball mill constructed in accordance with the first aspect 25 of the present invention. The milling was effected in a slight overpressure of pure, dry helium.

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In a first experiment, using crystallised ribbon that had been annealed for 10 minutes at 600°C, x-ray diffraction analysis of the milled product showed that after 90 hours of milling, the product had a 5 fully amorphous structure. (Before the milling, only a crystalline structure was revealed by the x-ray diffraction analysis.)

In a second experiment, using crystallised ribbon that had been annealed for 20 minutes at 600°C, x-ray 10 diffraction analysis after 250 hours of milling showed that re-amorphization of the ribbon had not been fully achieved. It is believed that the incomplete re-amorphization was due to the grain size of the starting material exceeding the diffusing 15 range that can be achieved during the ball milling process.

A secondary wet milling of samples of the fully re-amorphized powder, which had a particle size of from 5 to 20 micrometres, was then performed with an 20 appropriate surfactant added to the ball mill charge. The secondary milling reduced the particle size so that it was in the range of from 1 micrometre to 10 micrometres. This reduction in particle size was accompanied by an increase in the magnetic 25 permeability and the remanent magnetisation of the powder, with a decrease in its coercivity.

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Those familiar with mechanical grinding and alloying techniques will appreciate that in the above description, specific embodiments of each aspect of the present invention have been described. However, 5 modifications to those embodiments can be made without departing from the present inventive concept.

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CLAIMS

1. A ball mill comprising:

- (a) a substantially spherical or generally cylindrical chamber (20), the chamber being mounted (i) in the case of a substantially spherical chamber, for rotation about a substantially horizontal axis (21), and (ii) in the case of a generally cylindrical chamber, with the axis (21) of the cylinder substantially horizontal and for rotation about the axis of the cylinder; and
- (b) a plurality of steel balls (22) within the chamber;

characterised in that

- (c) the chamber is made of a paramagnetic material;
- (d) the material of which the balls are made is a ferromagnetic; and
- (e) at least one magnet (24) is mounted outside the chamber, said or each magnet (i) having lines of magnetic force which penetrate into the chamber, and (ii) being moveable between a plurality of locations along an arc having its centre of curvature substantially at the axis of rotation of the chamber.

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2. A ball mill as defined in claim 1, in which said or each magnet (24) is mounted for movement along an or a respective arc (25), said or each arc having its centre of curvature substantially at the axis of rotation of the chamber.
3. A ball mill as defined in claim 1, in which said or each magnet (24) is repositionable at a plurality of discrete locations and around the chamber, each one of the discrete locations being on an arc (25) having its centre of curvature substantially at the axis of rotation of the chamber.
4. A ball mill as defined in claim 1, claim 2 or claim 3, in which said or each magnet (24) is an electromagnet.
5. A ball mill as defined in claim 4, including means to vary the strength of the or each electromagnet.
6. A ball mill as defined in claim 1, claim 2 or claim 3, in which said or each magnet (24) is a permanent magnet.
7. A ball mill as defined in any preceding claim, including heating means for heating the chamber and its contents.

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8. A method of wet ball milling a material in a ball mill, characterised by the addition to the material of sufficient surfactant to coat the surface of the material with a monomolecular layer of the surfactant.
9. A method as defined in claim 8, in which the surfactant is added to the chamber of the ball mill together with a quantity of an organic solvent.
10. A method as defined in claim 9, in which the organic solvent is hexane.
11. A method as defined in claim 8, claim 9 or claim 10, in which the surfactant is a surfactant selected from the group consisting of
 - (a) sodium-1,2 bis (dodecyl carbonyl) ethane-1-sulfonate;
 - (b) lithium-1,2 bis dodecyloxycarbonyl sulfasuccinate;
 - (c) didodecyldimethyl ammonium bromide;
and
 - (d) ammonium dihexadecyl dimethylacetate.
12. A method for producing a metallic amorphous material, said method comprising the steps of:

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- (a) making a master alloy having the same chemical composition as the required metallic material; and
 - (b) producing amorphous ribbons of the master alloy;
- and characterised by the steps of
- (c) annealing the amorphous ribbons to convert them into crystalline form; then
 - (d) ball milling the crystalline material for a period sufficient to produce a fully amorphous powder.
13. A method as defined in claim 12, in which the annealing step is performed under vacuum at a temperature of about 600°C.
14. A method as defined in claim 13, in which the temperature of 600°C is maintained for a period in the range of from 10 minutes to 20 minutes.
15. A method as defined in claim 12, claim 13 or claim 14, in which the ball milling of the crystalline material is effected in an atmosphere comprising a slight overpressure of inert gas.
16. A method as defined in any one of claims 8 to 15, in which the ball milling is effected in a ball mill as defined in any one of claims 1 to 7.

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17. A ball mill substantially as hereinbefore described with reference to Figures 2 to 6 of the accompanying drawings.
18. A method of wet ball milling with the addition of a surfactant as defined in claim 8, substantially as hereinbefore described.
19. A method for producing a metallic amorphous material as defined in claim 12, substantially as hereinbefore described.

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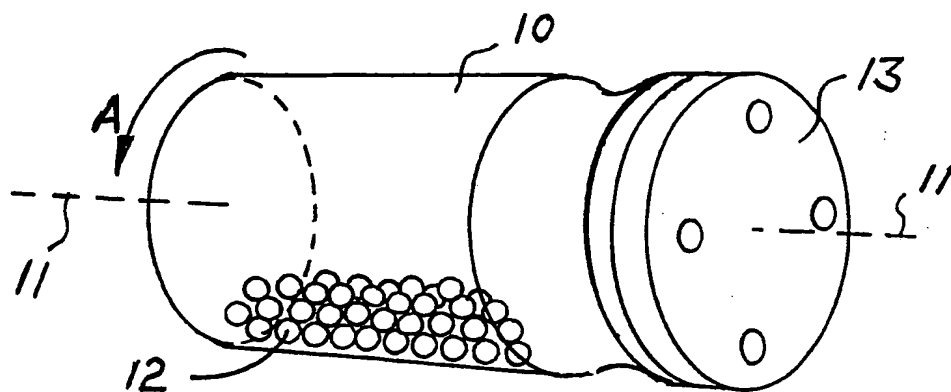


FIG. 1.

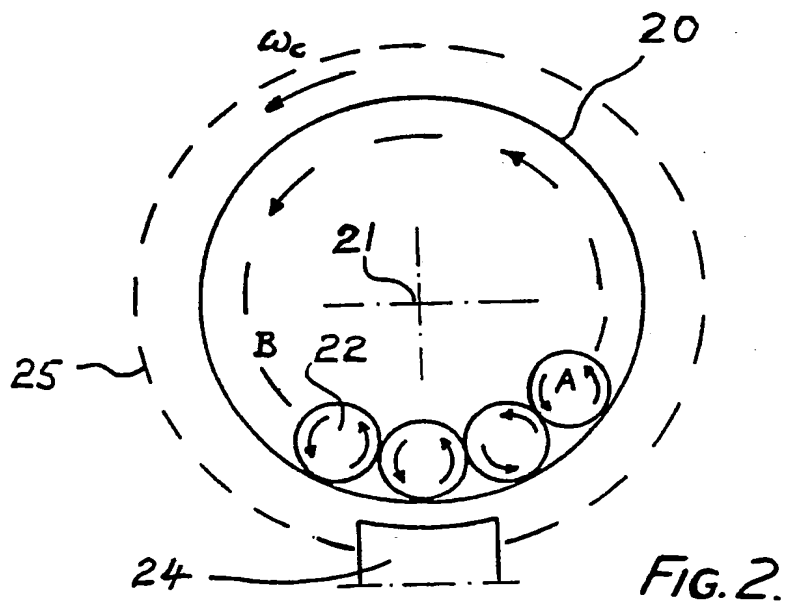


FIG. 2.

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FIG. 3.

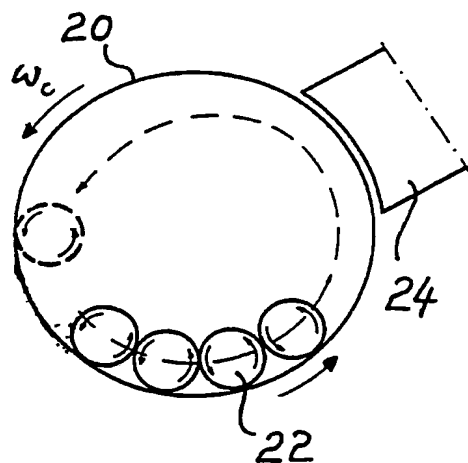
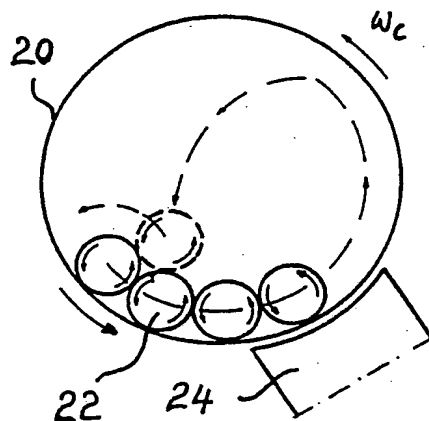
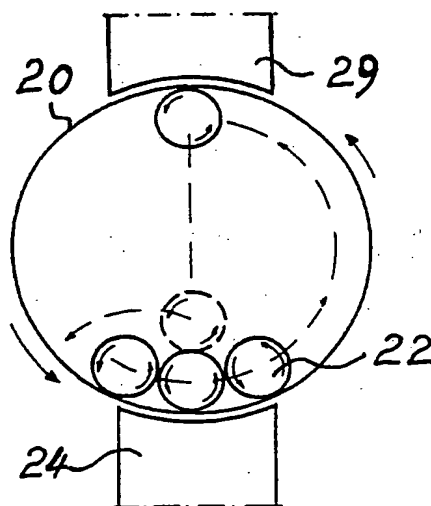


FIG. 4.

FIG. 5.



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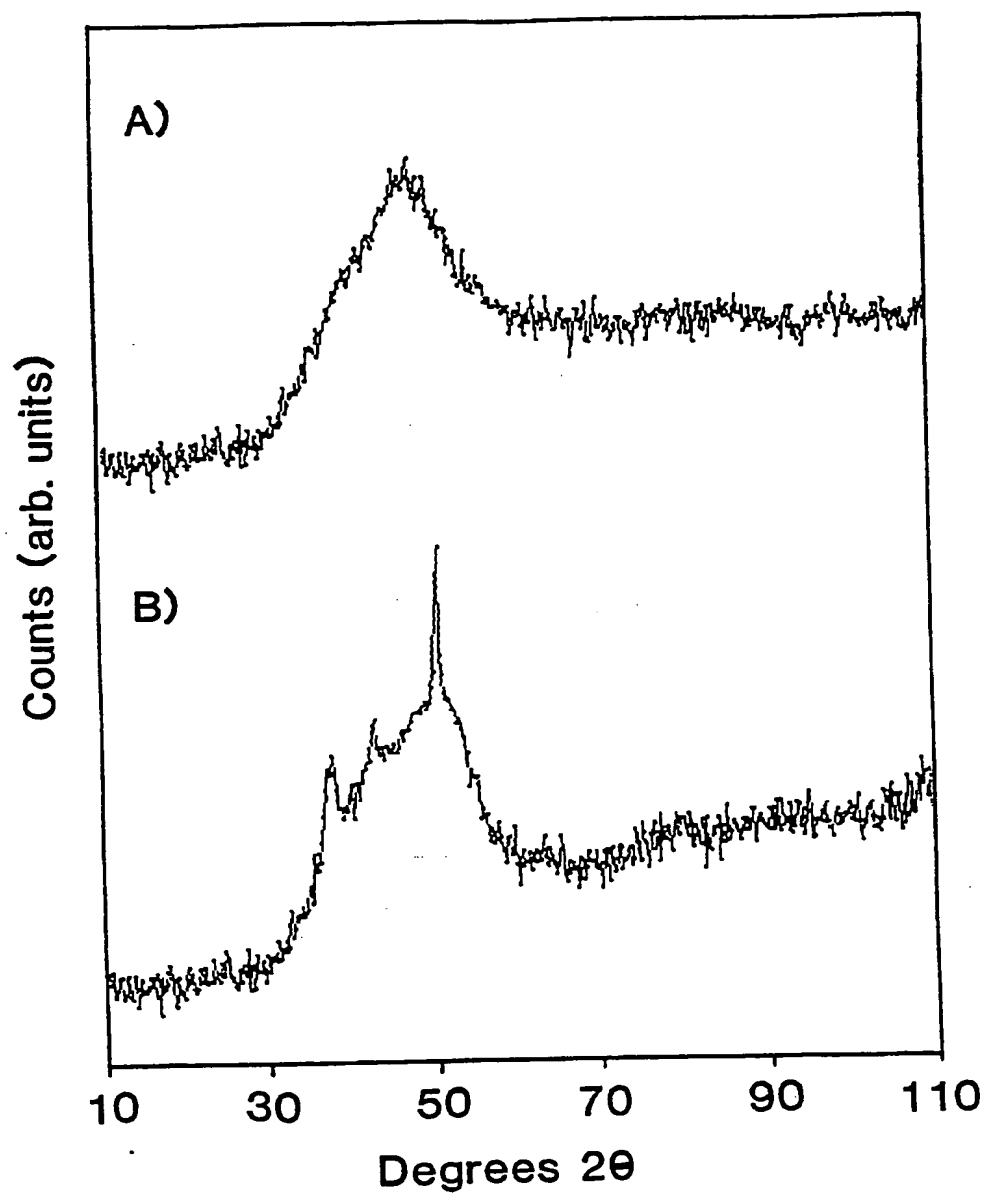


FIG. 6.

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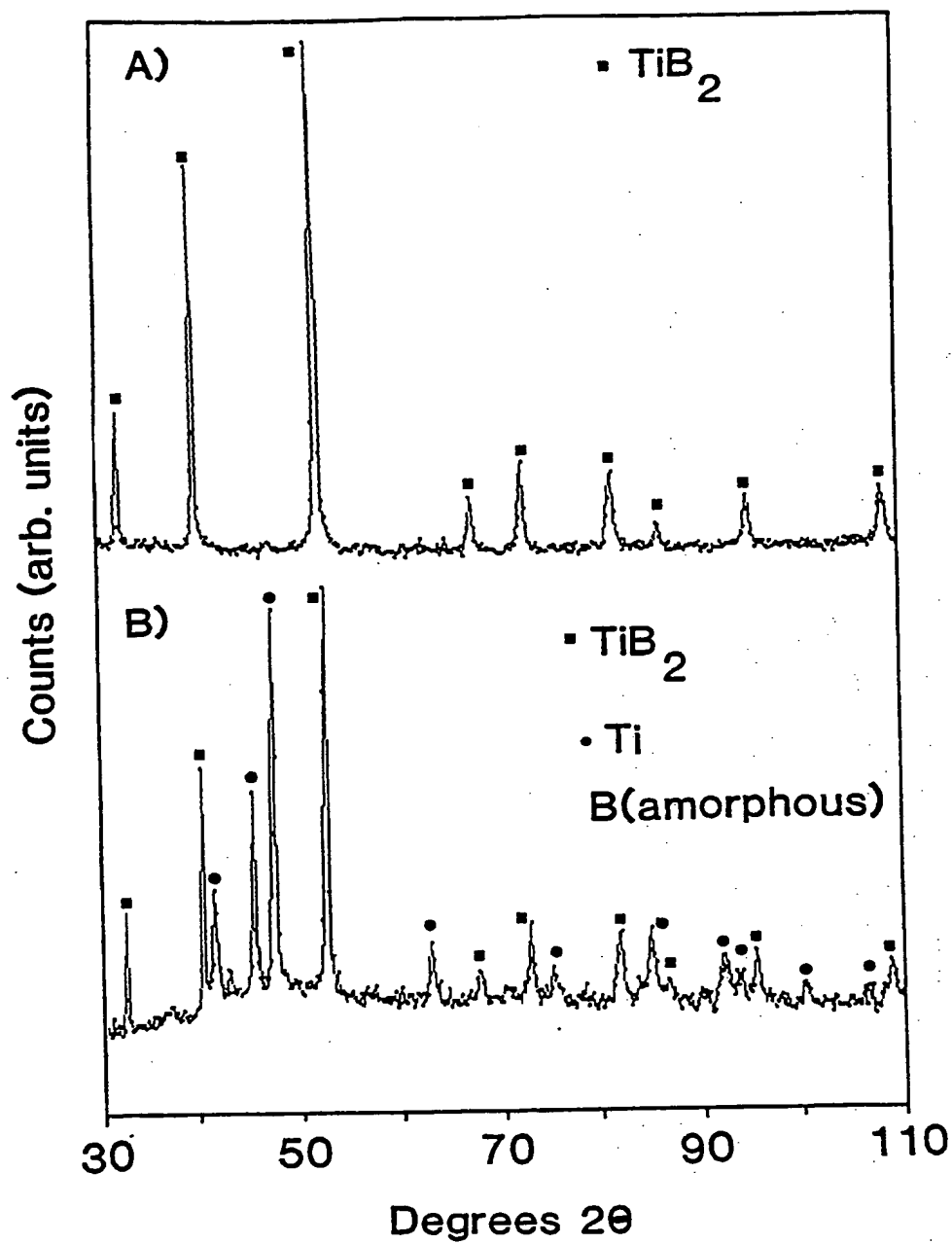
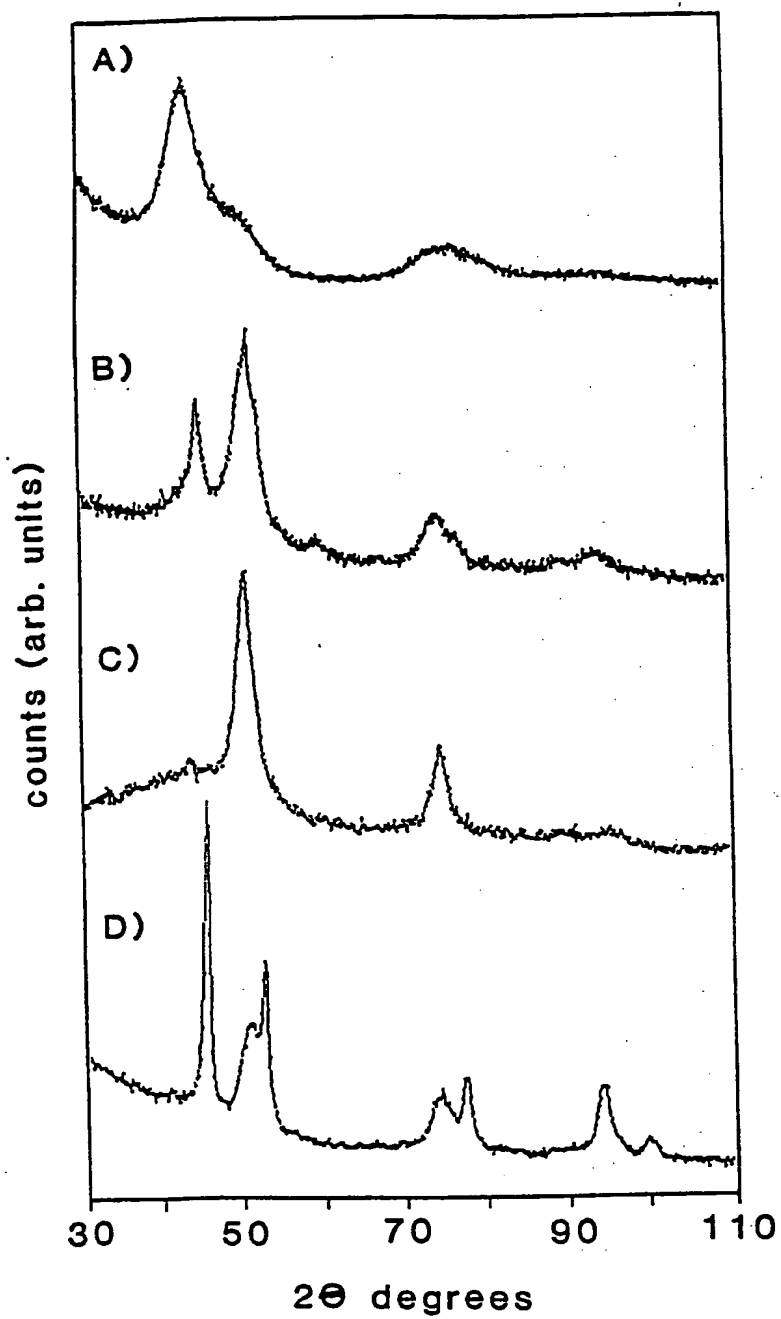


FIG. 7

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5/5*Fig. 8.*

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INTERNATIONAL SEARCH REPORT

International Application No. **PCT/AU 90/00471**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶				
According to International Patent Classification (IPC) or to both National Classification and IPC				
Int. Cl. ⁵ B22F 9/04, B02C 17/04 // C22C 45/00, C22F 1/02, B02C 17/00				
II. FIELDS SEARCHED				
Minimum Documentation Searched ⁷				
Classification System	Classification Symbols			
IPC	B02C 17/04, B02C 17/00, B22F 9/04, C22C 45/00, C22F 1/02			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸				
AU : IPC as above				
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹				
Category*	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No ¹³		
X	US,A, 4676439 (SAITO et al) 30 June 1987 (30.06.87) See column 4 lines 54-66, claim 1	(1-5)		
X	US,A, 4737308 (PEARSON) 12 April 1988 (12.04.88) See abstract	(8,11)		
X	US,A, 4826630 (RADFORD et al) 2 May 1989 (02.05.89) See abstract	(8)		
Y	Patents Abstracts of Japan, Vol.11, No.255 (M-617) 19 August 1987 & JP,A, 62-60803 (KAWASAKI STEEL CORP.) 17 March 1987 (17.03.87)	(12)		
Y	EP,A, 301561 (TIK CORPORATION) 1 February 1989 (01.02.89) See page 8 lines 26-28,41	(12)		
X,Y	EP,A, 84113 (ALLIED CORPORATION) 27 July 1983 (27.07.83) See claims 1-8	(12)		
<p>* Special categories of cited documents: ¹⁰</p> <table style="width: 100%;"> <tr> <td style="width: 50%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%;"> <p>"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </td> </tr> </table>			<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>
<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>			
IV. CERTIFICATION				
Date of the Actual Completion of the International Search 28 November 1990 (28.11.90)	Date of Mailing of this International Search Report 5 December 1990			
International Searching Authority Australian Patent Office	Signature of Authorized Officer <i>R A Melvin</i> R.A. MELVIN			

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☒ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 90/00471

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members		
US	4676439	DE 3407608	JP 59160543	JP 59160544
US	4737308	CA 1065730		
US	4826630	AU 91005/82 DE 3248020 GB 2112560 JP 58118984 ZA 8208575	BE 895483 ES 518591 IL 67321 SE 8206704	CH 663680 FR 2522867 IT 1153916 US 4474728
EP	301561	US 4923533 JP 1173796	JP 1139702 JP 1175300	JP 1205404 JP 2032599
EP	84113	CA 1203662 US 4650130	DE 3269729 US 4783900	JP 58120703

END OF ANNEX